p-type doping of II-VI heterostructures from surface states: application to ferromagnetic $Cd_{1-x}Mn_xTe$ quantum wells

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We present a study of p-type doping of CdTe and $Cd_{1-x}Mn_xTe$ quantum wells from surface states. We show that this method is as efficient as usual modulation doping with nitrogen acceptors, and leads to hole densities exceeding 2×10^{11} cm^{-2}. Surface doping was applied to obtain samples with $Cd_{1-x}Mn_xTe$ quantum well with up to $x = 9.3\%$ containing hole gas. We could also increase the growth temperature up to 280°C, which results in sharper photoluminescence lines, when compared to the similar nitrogen doped samples. Carrier-induced ferromagnetism was observed in surface doped samples.

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Studies of carrier induced ferromagnetism in diluted magnetic semiconductors (DMS) are important for the development of spintronics - a new field exploiting spin degrees of freedom for information processing. The most conclusive results have been obtained for p-type doped structures. In III-V DMS, the same impurity (Mn) carries the localized spins and acts as an acceptor [?] which puts strong limits on the realization of QWs and 2D systems [?] using thin layers of III-V DMS [? ?]. In $Cd_{1-x}Mn_xTe$ quantum wells (QW), it has been proposed theoretically [?] and shown experimentally[?] that the presence of a two dimensional (2D) carrier gas can induce a ferromagnetic ordering due to the strong exchange coupling of Mn spins to charge carriers. In [?], the modulation-doped structures were grown by molecular beam epitaxy using nitrogen acceptors in the $Cd_{1-y-z}Zn_zMg_yTe$ barriers. Although efficient, this method brings certain restrictions. Effective doping of $Cd_{1-y-z}Zn_zMg_yTe$ with nitrogen is only possible for y lower than 30%, it requires lowering the growth temperature from the usual 280°C down to 220°C to avoid a strong interdiffusion of the heterostructure [?], and thus affects the quality of the samples, e.g., by increasing interface roughness [?]. Moreover the presence of nitrogen precludes almost any post-growth treatment of the sample.

In this letter we present a method of p-type doping of $Cd_{1-x}Mn_xTe$ QWs from surface states. We show that this method can be as efficient as modulation doping with nitrogen in supplying a hole gas to the QWs, and can be used to induce a ferromagnetic order in the QW. Furthermore it increases the thermal stability of structures allowing growth and processing of samples at higher temperature. Finally, it makes possible to obtain a hole gas in deeper quantum wells or quantum wells with a higher Mn content.

Samples have been grown by molecular-beam epitaxy on two types of (001) substrates, $Cd_{0.88}Zn_{0.12}Te$ which is transparent at the energy of the QW transition, and $Cd_{0.96}Zn_{0.04}Te$. For comparison purposes the growth parameters were first kept in the range typical for the growth of the nitrogen doped samples, including the substrate temperature 220°C. Each sample contained a 100Å wide QW made of $Cd_{1-x}Mn_xTe$ or CdTe. The QW was embedded between $Cd_{0.7}Zn_{0.08}Mg_{0.22}Te$ barriers in case of 12% Zn substrate and $Cd_{0.78}Mg_{0.22}Te$ for the samples grown on the 4% Zn substrate, so that the whole structure could be grown coherently strained to the substrate. The thickness of the top barrier was in the range from 150Å to 1000Å. The barrier on the substrate side was 3000Å thick.

All properties discussed below were determined by magneto-optical spectroscopy in the Faraday configuration (magnetic field perpendicular to the sample surface), with the sample mounted strain-free in liquid helium in a superconducting magnet. The experimental setup allowed us to perform transmission and reflectivity studies using a halogen lamp, and photoluminescence (PL) and PL excitation (PLE) using a tunable Al_2O_3:Ti laser providing about 2 mW/cm^2. The composition of barriers was checked from the PL transition energy [?]. The Mn content in the QW was checked from fitting a modified Brillouin function [?] to the Zeeman splitting measured in PL.

The first evidence for the presence of a carrier gas in a QW close to the surface comes from transmission spectra with applied magnetic field (Fig. 1a). Two narrow absorption lines are observed. Their splitting (about 3 meV) and the strong circular polarization of the low energy line are a fingerprint of a charged exciton transition, and therefore an indication of the presence of a carrier gas [? ? ?].

In a CdTe QW subject to a compressive biaxial strain, such as those here which were coherently grown on a $Cd_{0.88}Zn_{0.12}Te$ substrate, the sign of the charge carriers is

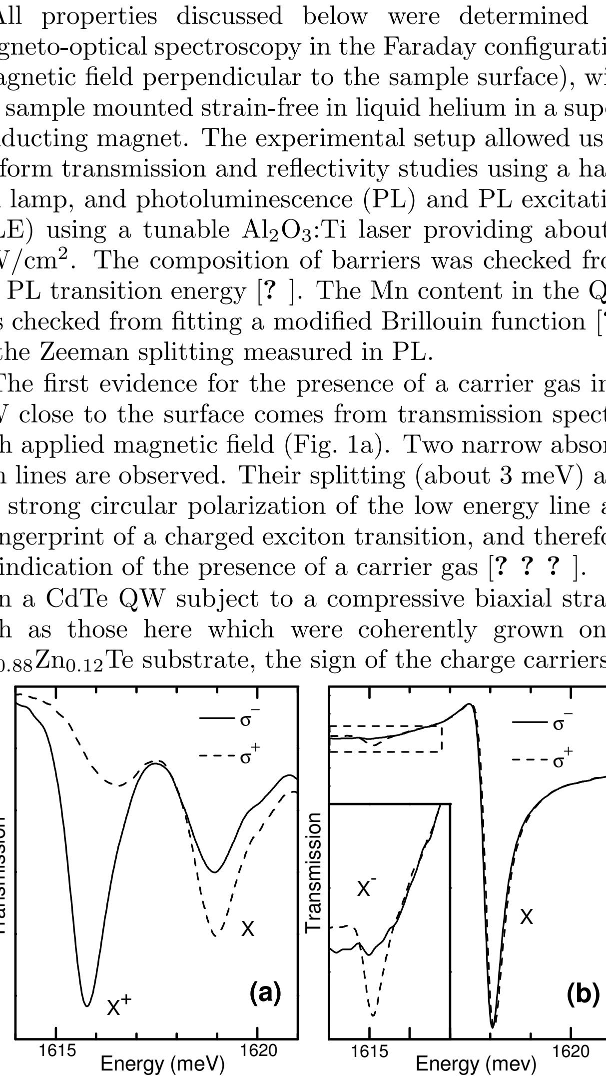

FIG. 1: Circularly polarized transmission spectra, at 3T and 1.7K, for a single CdTe QW with a cap layer thickness of (a) 250Å and (b) 1000Å. The inset in (b) presents a close-up of the area of the spectrum attributed to a negatively charged exciton. Note the change in lineshape which is consistent with the change in the cap layer thickness

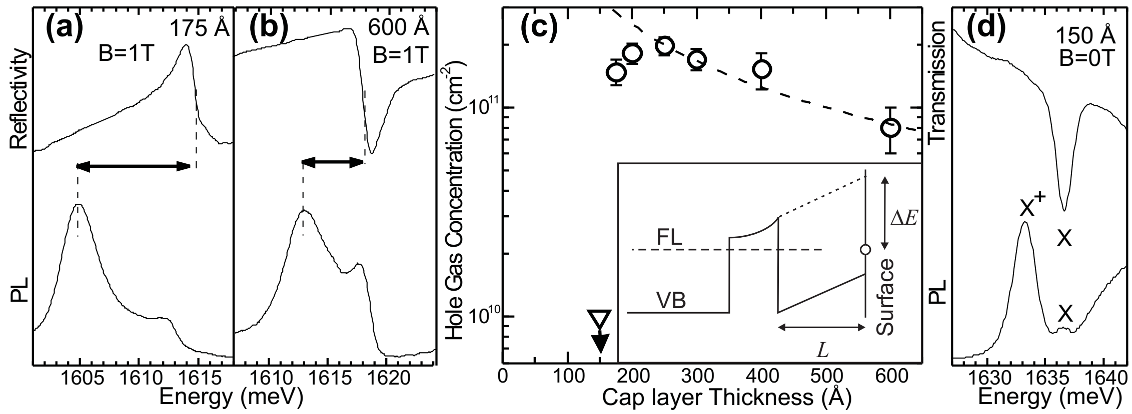

FIG. 2: **(a),(b)** Reflectivity (top) an PL spectra (bottom) at 1.7 K and 1 T for two $Cd_{0.99}Mn_{0.01}Te$ QWs with different cap layer thicknesses, as indicated. Arrows note the Moss-Burstein shift. **(c)** Hole density in 100Å wide $Cd_{0.99}Mn_{0.01}Te$ QWs, determined from the Moss-Burstein shift at 1T (circles) or from the charged exciton intensity (triangle, two samples). The dashed line is the density expected from surface acceptor states at energy $\Delta E = 90$meV from the QW state (model schematized in the inset: FL - Fermi level, VB - Valence band, L- distance of the acceptor sheet from the QW. **(d)** Transmission (top) and PL spectra (bottom) for a $Cd_{0.99}Mn_{0.01}Te$ QW with a 150Å thick cap layer. Neutral and charged exciton lines dominate the spectra indicating a low carrier density.

unambiguously determined from the circular polarization of the charged exciton absorption in Faraday configuration: Due to the same signs of the electron and hole g-factors, the positively charged exciton is observed in σ^- polarization[**?**] while the negatively charged exciton is observed in σ^+ polarization [**?**]. In Fig. 1a, the lower energy line obeys the selection rules for positively charged excitons, which shows that free holes are present in this CdTe QW close to the surface. Note that no nitrogen acceptors were introduced into this sample. The opposite polarization rule was observed in a CdTe QW identical to the previous one but with a thicker (1000Å) cap layer (Fig. 1b). The weak intensity of the X^- line indicates a low concentration of electrons. Hence we conclude that we have a weak residual doping, which is n-type and accounts for the low electron density in the deeply buried QW, while the hole gas with a higher density in the QW close to the surface has a different origin.

The presence of a carrier gas was also evidenced in $Cd_{1-x}Mn_xTe$ QWs. In samples with a thin cap layer, the so-called Moss-Burstein shift between the absorption (or reflectivity or PLE) line and the PL line indicates a large density of carriers in the QW (Fig. 2a, b). In the

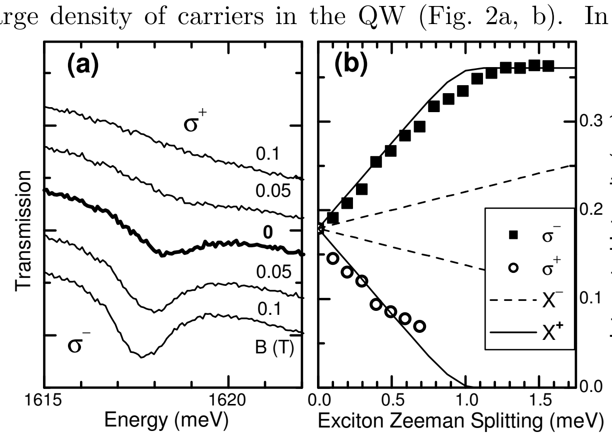

FIG. 3: **(a)** Transmission spectra, in magnetic field, for a $Cd_{0.995}Mn_{0.005}Te$ QW placed 250Å below the surface of the sample. Measured hole concentration is $2\times10^{-11}\text{cm}^{-2}$. **(b)** Integrated intensity of transmission line versus Zeeman splitting in both circular polarizations (points) and results of calculation for electron (solid line) and hole gases (dashed line).

case of band-to-band transitions, the Moss-Burstein shift is equal to the sum of the kinetic energies of electrons and holes (which are involved in the excitation process) at Fermi wavevector k_F, so that it can be used as a tool for measuring the carrier density. For a better accuracy, the Moss-Burstein shift was measured at a magnetic field such that the carrier gas was fully polarized: Then the Moss-Burstein shift measured in σ^+ polarization is twice its value at zero field. Note the change in reflectivity line in agreement with the cap layer thickness [**?**]. The carrier density was then calculated assuming an effective electron mass $m_e^* = 0.1m_0$, and an in-plane hole mass $m_h^* = 0.25m_0$ [**?**]. We estimate that the relative carrier concentration is then determined to within a few %, while its absolute value is accurate to within a factor of two due to residual excitonic effects [**?**]. The determination of the carrier density from the Moss-Burstein shift makes no assumption on the nature (electrons or holes) of the carriers. However, once the density of carriers is known, their sign can be deduced from the value of the magnetic field necessary to fully polarize the carrier gas. Full polarization is witnessed by the vanishing of the charged exciton absorption in σ^+ polarization(Fig. 3). Due to the giant Zeeman effect, characteristic for diluted magnetic semiconductors (DMS), complete spin polarization of a hole gas of density $2\times10^{-11}\text{cm}^{-2}$ in a $Cd_{0.99}Mn_{0.01}Te$ QW is achieved when applying a magnetic field as low as 0.1T. This field is expected to be at least 5 times larger for the same density of electrons[**? ?**].

A set of samples with similar growth conditions, and almost identical structure, allowed us to investigate the influence of the cap layer thickness on the QW hole density. In this series of samples, contrary to samples shown in Fig. 1, we used a thin layer of nitrogen doped barrier material, 1000Å below the QW, to screen any spurious effect from the interface with the substrate. The hole density (as deduced from the Moss-Burstein shift) significantly increases when the thickness of the cap layer decreases from 600 to 250Å (Fig. 2c). This reinforces the idea that the origin of the hole gas is not linked to a residual doping of the material, but is due to the presence of electron traps (acceptors) on the surface. We can calculate the hole density expected in the QW assuming a high density of acceptor states on

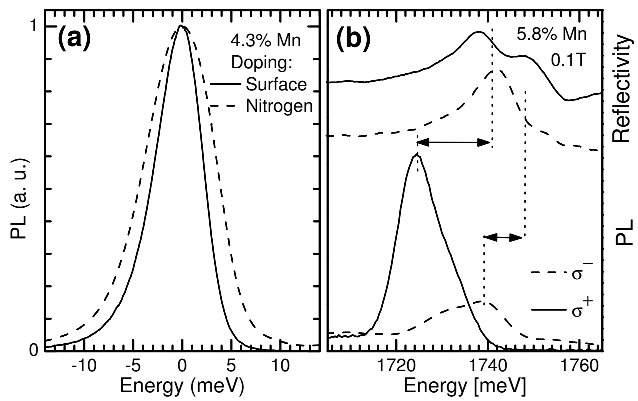

FIG. 4: **(a)** Zero field PL spectra of a single $Cd_{0.957}Mn_{0.043}Te$ QW at 4.2K. The QW is depleted from carriers using blue light illumination. One sample (dashed line) was grown at 220°C and doped with nitrogen. The other one was doped from the surface states (250Å cap layer) and grown at 280°C. Both have the same Mn content and carrier density in the dark. The spectra are normalized and their positions are shifted. **(b)** PL and reflectivity spectra in circular polarizations at 0.1T and 1.7K for a sample with 5.8%Mn in the QW.

the surface, with the energy position of these surface states as the only adjustable parameter. If we define this position by the distance ΔE between the acceptor state and the level confined in the QW, the hole density is mostly determined by the effect of the electric field between the QW and the surface (see the inset in Fig. 2c), *i.e.* we can neglect small contributions such as the change of confinement energy within the QW, the kinetic energy of confined carriers, or the valence band shift due to the small amount of Mn in the QW. Then the QW hole density simply writes $p = \varepsilon\varepsilon_0\Delta E/(eL)$ where ε (=10) is the dielectric constant of the cap material, ε_0 is the permittivity of vacuum, e is the electron charge, and L is the thickness of the cap layer. A good fit is obtained if we take $\Delta E = 90$ meV (dashed curve in Fig. 2c).

This value should be considered with care. First the carrier density is probably higher than the value we determine optically, since illumination tends to decrease the carrier density, even when using a low intensity at photon energy smaller than the barrier gap. In addition, one should keep in mind that - due to residual excitonic effects - the Moss-Burstein shift determination is not too precise on the absolute value of the carrier density[**?**]. Also, a drop of the carrier density is observed on the samples with a very thin cap layer (below 200Å). The decrease is dramatic in the two samples grown with $L = 150$Å, where the free exciton is observed in transmission (Fig. 2d), so that we estimate the carrier density to be smaller than $10^{-10}\mathrm{cm}^{-2}$ [**?**]. Further studies are needed to elucidate the origin of this sharp drop.

The main result is that we obtained hole densities exceeding $2 \times 10^{11}\mathrm{cm}^{-2}$ in the QWs with a cap layer thickness of 250Å without using impurities. The presence of holes probably also explains PL spectra observed in nominally undoped parts of gradually doped samples [**?**]. We show now that this allows us to increase the growth temperature and to grow DMS QWs with a higher Mn content than our previous upper limit (below $x = 0.05$).

Undoped samples have been shown to exhibit sharper lines when grown at higher temperatures [**?**] due to reduction of interface roughness. In doped samples other cases of broadening can operate. However in figure 4a we compare PL spectra of a nitrogen doped sample grown at 220°C, and of a sample doped from the surface states and grown at 280°C. Both samples contain 4.3% Mn in the QW, and identical carrier densities in the dark. We present spectra measured in zero magnetic field and under blue illumination in order to deplete the QW from hole gas. Sharper lines are observed in the second sample.

Carrier induced ferromagnetism was observed in those samples with 4.3% Mn [**?**], with the same behavior in the nitrogen and surface doped samples. In addition, we can grow $Cd_{1-x}Mn_xTe$ QWs with the x up to 9.3% and yet a significant hole density. As an example figure 4b presents the PL and reflectivity spectra in circular polarizations for a sample with 5.8% Mn in the QW at magnetic field of 0.1T, so that the hole gas is fully polarized. The shift in σ^- polarization can be attributed to disorder (Stokes shift). The shift in σ^+ polarization is significantly higher due to the presence of the hole gas and accompanying Moss-Burstein shift.

We have no conclusive information on the nature of the surface states involved in the formation of the hole gas. The presence of acceptor states at the surface of $Cd_{1-x}Zn_xTe$ has been reported by Yang et al. [**?**] and attributed to the formation of TeO_2. In order to control the formation of oxides on the $Cd_{1-y-z}Mg_yZn_zTe$ surface, a 50Å thick layer of amorphous tellurium can be deposited at –20°C right after the growth. We used two samples placed side-by-side on the substrate holder during the growth. Then one sample was removed from the MBE chamber, and the second one was heated up to 240°C for a few seconds in the vacuum, in order to re-evaporate the Te layer (as controlled by RHEED). No hole gas was present in the QW of the sample protected by the Te layer, while a hole density $2 \times 10^{11}cm^{-2}$ was found in the QW of the sample without the Te cap. This suggests that surface oxides may indeed play a role in the formation of the electron traps.

In conclusion, we demonstrate an efficient method for doping CdTe QWs using surface acceptor states. Hole densities in excess of 2×10^{11} cm^{-2} in the QW have been measured by optical spectroscopy. The investigated mechanism was applied to obtain samples containing up to 9.3% Mn in the QW with a significant hole gas density. Efficient doping can be achieved without the technological restrictions arising from incorporating nitrogen impurities into the structures. We can therefore use higher temperatures for the growth of the samples (and further processing) and obtain a hole gas in deeper quantum wells or quantum wells with a higher Mn content.

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